

ANTIMICROBIAL CLEANING COMPOSITION

Field of the Invention

The present invention relates to an antimicrobial cleaning composition for
5 cleaning surfaces which provides a lasting antibacterial protection on the surface being
cleaned, wherein the composition includes polyhexamethylene biguanide hydrochloride
complexed with an anionic a surfactant and water.

Background of the Invention

Poly (hexamethylene biguanide) hydrochloride has been used in the food
10 industry as an antibacterial solution for equipment disinfection but these solutions
exhibit poor substantivity.

Numerous cleaning compositions have been disclosed in various patents. These
cleaning compositions deliver instant bacteria killing efficacy on the treated surface.
However, a major problem is that these antimicrobial solutions show poor substantivity
15 in that, once bacteria are killed, no lasting protection is provided on the treated or
cleaned surface against the future growth of new coming bacteria.

Poly (hexamethylene biguanide) hydrochloride has been used in combination
with a cationic surfactant such as didecyl dimethyl ammonium chloride in laundry
compositions but the substantivity of these laundry compositions is inferior.

20 Patent applications WO99/40791 and EPO891712A1 comprises a substantive
antibacterial solution containing silver ions, poly (hexamethylene biguanide)
hydrochloride which is crosslinked by sodium lauryl sulfate.

Avecia Limited of England also provides poly (hexamethylene biguanide)
stearate for soap bars.

25 The exploitation of interpolyelectrolyte reaction (PHMB with polyacrylic acid) has
already been exploited to prepare antimicrobial fibres, but in this case the anionic
polymer was chemically grafted on the cellulose (Virnik A.D., Penenzhik M.A., Grishin
M.A., Rishkina I.S., Zezin A.B., Rogacheva V.B. 1994. Interpolyelectrolyte reactions
between polyhexamethylene guanidine and polyacrylic acid grafted on cellulose: a new

method for the preparation of antimicrobial fibrous material. Cellulose Chem. Technol. 28, 11-19).

Summary of the Invention

The present invention relates to an antimicrobial cleaning composition having improved substantivity which comprises a complex of polyhexamethylene biguanide hydrochloride and an anionic surfactant selected from the group consisting of alkyl sulfates, ethoxylated alkyl ether sulfates, paraffin sulfonates, alpha olefin sulfonates and linear alkyl benzene sulfonates and mixtures thereof, and water, wherein the composition does not contain a polyethylene oxide polycarboxylate copolymer, an anionic biopolymer, silicon containing polymer, amino containing polymers, copolymers of polyvinyl pyrrolidone or polyvinyl pyrridine N-oxide polymers.

It is an object of the instant invention to provide an antibacterial cleaning composition, wherein the anionic surfactants links with the polyhexamethylene biguanide hydrochloride thereby improving the deposition and the resistance to rinse off of the polyhexamethylene biguanide hydrochloride from the surface being cleaned, wherein the composition provides lasting antibacterial protection for the hard surface which has been treated.

Detailed Description of the Invention

The present invention relates to a hard surface cleaning composition which renders the surface being treated resistant to the growth of bacteria, wherein the composition comprises approximately by weight:

- (a) 0.01 to 10%, more preferably 0.01% to 5% of at least one anionic surfactant;
- (b) 0.01% to 5%, more preferably 0.01% to 1% of polyhexamethylene biguanide hydrochloride;
- (c) 0 to 10%, more preferably 0.1 wt. % to 5 wt. % of a second surfactant selected from the group consisting of ethoxylated nonionic surfactants, amine oxides, alkyl polyglucosides and zwitterionic surfactants and mixtures thereof; and

(d) the balance being water, wherein the composition does not contain an amino containing polymer, a polyethylene oxide polycarboxylate copolymer, a silicon containing polymer, a cationic surfactant, a copolymer of polyvinyl pyrrolidone or polyvinyl pyrridine N-oxide polymers.

5 Regarding the anionic surfactant which is present in the compositions can be any of the conventionally used water-soluble anionic surfactants or mixtures of said anionic surfactants can be used in this invention. As used herein the term "anionic surfactant" is intended to refer to the class of anionic and mixed anionic-nonionic detergents providing deterative action.

10 Suitable water-soluble non-soap, anionic surfactants include those surface-active or detergent compounds which contain an organic hydrophobic group containing generally 8 to 26 carbon atoms and preferably 10 to 18 carbon atoms in their molecular structure and at least one water-solubilizing group selected from the group of sulfonate, sulfate and carboxylate so as to form a water-soluble detergent. Usually, the
15 hydrophobic group will include or comprise a C₈-C₂₂ alkyl, alkyl or acyl group. Such surfactants are employed in the form of water-soluble salts and the salt-forming cation usually is selected from the group consisting of sodium, potassium, ammonium, magnesium and mono-, di- or tri-C₂-C₃ alkanolammonium, with the sodium, magnesium and ammonium cations again being preferred.

20 The anionic surfactants which is used in the composition of this invention are water soluble and include the sodium, potassium, ammonium and ethanolammonium salts of linear C₈-C₁₆ alkyl benzene sulfonates, alkyl ether carboxylates, C₁₀-C₂₀ paraffin sulfonates, C₈-C₂₅ alpha olefin sulfonates, C₈-C₁₈ alkyl sulfates, alkyl ether sulfates and mixtures thereof.

25 The paraffin sulfonates may be monosulfonates or di-sulfonates and usually are mixtures thereof, obtained by sulfonating paraffins of 10 to 20 carbon atoms. Preferred paraffin sulfonates are those of C₁₂-18 carbon atoms chains, and more preferably they are of C₁₄-17 chains. Paraffin sulfonates that have the sulfonate group(s) distributed along the paraffin chain are described in U.S. Patents 2,503,280; 2,507,088; 3,260,744;

and 3,372,188; and also in German Patent 735,096. Such compounds may be made to specifications and desirably the content of paraffin sulfonates outside the C₁₄₋₁₇ range will be minor and will be minimized, as will be any contents of di- or poly-sulfonates.

Examples of suitable other sulfonated anionic detergents are the well known higher alkyl mononuclear aromatic sulfonates, such as the higher alkylbenzene sulfonates containing 9 to 18 or preferably 9 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, or C₈₋₁₅ alkyl toluene sulfonates. A preferred alkylbenzene sulfonate is a linear alkylbenzene sulfonate having a higher content of 3-phenyl (or higher) isomers and a correspondingly lower content (well below 50%) of 2-phenyl (or lower) isomers, such as those sulfonates wherein the benzene ring is attached mostly at the 3 or higher (for example 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Preferred materials are set forth in U.S. Patent 3,320,174, especially those in which the alkyls are of 10 to 13 carbon atoms.

Other suitable anionic surfactants are the olefin sulfonates, including long-chain alkene sulfonates, long-chain hydroxyalkane sulfonates or mixtures of alkene sulfonates and hydroxyalkane sulfonates. These olefin sulfonate detergents may be prepared in a known manner by the reaction of sulfur trioxide (SO₃) with long-chain olefins containing 8 to 25, preferably 12 to 21 carbon atoms and having the formula RCH=CHR₁ where R is a higher alkyl group of 6 to 23 carbons and R₁ is an alkyl group of 1 to 17 carbons or hydrogen to form a mixture of sultones and alkene sulfonic acids which is then treated to convert the sultones to sulfonates. Preferred olefin sulfonates contain from 14 to 16 carbon atoms in the R alkyl group and are obtained by sulfonating an α -olefin.

Examples of satisfactory anionic sulfate surfactants are the alkyl sulfate salts and the alkyl ether polyethenoxy sulfate salts having the formula R(OC₂H₄)_nOSO₃M wherein n is 1 to 12, preferably 1 to 5, and R is an alkyl group having about 8 to about 18 carbon atoms, more preferably 12 to 15 and natural cuts, for example, C₁₂₋₁₄ or C₁₂₋₁₆ and M is a solubilizing cation selected from the group consisting of

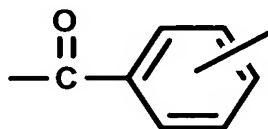
sodium, potassium, ammonium, magnesium and mono-, di- and triethanol ammonium ions. The alkyl sulfates may be obtained by sulfating the alcohols obtained by reducing glycerides of coconut oil or tallow or mixtures thereof and neutralizing the resultant product.

5 The ethoxylated alkyl ether sulfate may be made by sulfating the condensation product of ethylene oxide and C₈-18 alkanol, and neutralizing the resultant product.

The ethoxylated alkyl ether sulfates differ from one another in the number of carbon atoms in the alcohols and in the number of moles of ethylene oxide reacted with one mole of such alcohol. Preferred alkyl ether sulfates contain 12 to 15 carbon atoms in
10 the alcohols and in the alkyl groups thereof, e.g., sodium myristyl (3 EO) sulfate.

Ethoxylated C₈-18 alkylphenyl ether sulfates containing from 2 to 6 moles of ethylene oxide in the molecule are also suitable for use in the invention compositions. These detergents can be prepared by reacting an alkyl phenol with 2 to 6 moles of ethylene oxide and sulfating and neutralizing the resultant ethoxylated alkylphenol.

15 Other suitable anionic detergents are the C₉-C₁₅ alkyl ether polyethenoxy carboxylates having the structural formula $R(OC_2H_4)_nOX$ COOH wherein n is a number from 4 to 12, preferably 6 to 11 and X is selected from the group consisting of CH₂, C(O)R₁ and



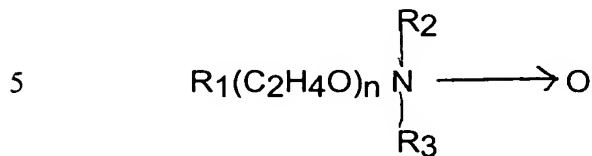
20 wherein R₁ is a C₁-C₃ alkylene group. Preferred compounds include C₉-C₁₁ alkyl ether polyethenoxy (7-9) C(O) CH₂CH₂COOH, C₁₃-C₁₅ alkyl ether polyethenoxy (7-9)



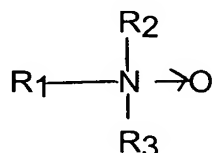
and C₁₀-C₁₂ alkyl ether polyethenoxy (5-7) CH₂COOH. These compounds may be prepared by condensing ethylene oxide with appropriate alkanol and reacting this
25 reaction product with chloracetic acid to make the ether carboxylic acids as shown in US Pat. No. 3,741,911 or with succinic anhydride or phthalic anhydride.

Obviously, these anionic detergents will be present either in acid form or salt form depending upon the pH of the final composition.

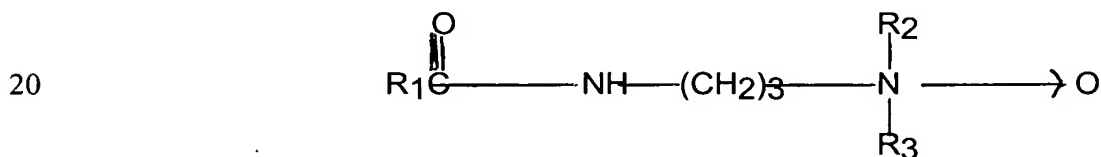
The amine oxide is depicted by the formula:



wherein R₁ is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, contain from about 8 to about 18 carbon atoms; R₂ and R₃ are each methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl; and n is from 0 to about 10. Particularly preferred are amine oxides of the formula:



wherein R₁ is a C₁₂-18 alkyl and R₂ and R₃ are methyl or ethyl. The above ethylene oxide condensates, amides, and amine oxides are more fully described in U.S. Patent No. 4,316,824 (Pancheri), incorporated herein by reference. An especially preferred amine oxide is depicted by the formula:



wherein R₁ is a saturated or unsaturated alkyl group having about 6 to about 24 carbon atoms, R₂ is a methyl group, and R₃ is a methyl or ethyl group. The preferred amine oxide is cocoamidopropyl-dimethylamine oxide.

25 The water soluble nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates and ethylene-oxide-propylene oxide condensates on primary alkanols, such as Plurafacs (BASF) and condensates of ethylene oxide with sorbitan fatty acid esters such as the Tweens (ICI). The nonionic

synthetic organic detergents generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water-soluble nonionic detergent. Further, the length of the polyethenoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

The nonionic surfactant class includes the condensation products of a higher alcohol (e.g., an alkanol containing about 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with about 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with about 16 moles of ethylene oxide (EO), tridecanol condensed with about 6 to moles of EO, myristyl alcohol condensed with about 10 moles of EO per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to about 14 carbon atoms in length and wherein the condensate contains either about 6 moles of EO per mole of total alcohol or about 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing about 9-15 carbon atoms, such as C₉-C₁₁ alkanol condensed with 2.5 to 10 moles of ethylene oxide (NEODOL 91-2.5 OR -5 OR -6 OR -8), C₁₂-13 alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C₁₂-15 alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C₁₄-15 alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like.

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene

oxide. Examples of commercially available nonionic detergents of the foregoing type are C₁₁-C₁₅ secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

Other suitable nonionic surfactants include the polyethylene oxide condensates of one mole of alkyl phenol containing from about 8 to 18 carbon atoms in a straight- or branched chain alkyl group with about 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl phenol condensed with about 9.5 moles of EO per mole of nonyl phenol, dinonyl phenol condensed with about 12 moles of EO per mole of phenol, dinonyl phenol condensed with about 15 moles of EO per mole of phenol and di-isooctylphenol condensed with about 15 moles of EO per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630 (nonyl phenol ethoxylate) marketed by GAF Corporation.

Also among the satisfactory nonionic surfactants are the water-soluble condensation products of a C₈-C₂₀ alkanol with a heteric mixture of ethylene oxide and propylene oxide wherein the weight ratio of ethylene oxide to propylene oxide is from 2.5:1 to 4:1, preferably 2.8:1 to 3.3:1, with the total of the ethylene oxide and propylene oxide (including the terminal ethanol or propanol group) being from 60-85%, preferably 70-80%, by weight. Such detergents are commercially available from BASF-Wyandotte and a particularly preferred detergent is a C₁₀-C₁₆ alkanol condensate with ethylene oxide and propylene oxide, the weight ratio of ethylene oxide to propylene oxide being 3:1 and the total alkoxy content being about 75% by weight.

Condensates of 2 to 30 moles of ethylene oxide with sorbitan mono- and tri-C₁₀-C₂₀ alkanolic acid esters having a HLB of 8 to 15 also may be employed as the nonionic detergent ingredient in the described composition. These surfactants are well known and are available from Imperial Chemical Industries under the Tween trade name. Suitable surfactants include polyoxyethylene (4) sorbitan monolaurate, polyoxyethylene (4) sorbitan monostearate, polyoxyethylene (20) sorbitan trioleate and polyoxyethylene (20) sorbitan tristearate.

Other suitable water-soluble nonionic surfactants are marketed under the trade name "Pluronics". The compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion of the molecule is of the order of 950 to 4000 and preferably 200 to 2,500. The addition of polyoxyethylene radicals to the hydrophobic portion tends to increase the solubility of the molecule as a whole so as to make the surfactant water-soluble. The molecular weight of the block polymers varies from 1,000 to 15,000 and the polyethylene oxide content may comprise 20% to 80% by weight. Preferably, these surfactants will be in liquid form and satisfactory surfactants are available as grades L 62 and L 64.

The alkyl polysaccharides surfactants, which are used in the instant composition with the aforementioned surfactants have a hydrophobic group containing from about 8 to about 20 carbon atoms, preferably from about 10 to about 16 carbon atoms, most preferably from about 12 to about 14 carbon atoms, and polysaccharide hydrophilic group containing from about 1.5 to about 10, preferably from about 1.5 to about 4, most preferably from about 1.6 to about 2.7 saccharide units (e.g., galactoside, glucoside, fructoside, glucosyl, fructosyl; and/or galactosyl units). Mixtures of saccharide moieties may be used in the alkyl polysaccharide surfactants. The number x indicates the number of saccharide units in a particular alkyl polysaccharide surfactant. For a particular alkyl polysaccharide molecule x can only assume integral values. In any physical sample of alkyl polysaccharide surfactants there will be in general molecules having different x values. The physical sample can be characterized by the average value of x and this average value can assume non-integral values. In this specification the values of x are to be understood to be average values. The hydrophobic group (R) can be attached at the 2-, 3-, or 4- positions rather than at the 1-position, (thus giving e.g. a glucosyl or galactosyl as opposed to a glucoside or galactoside). However, attachment through the 1- position, i.e., glucosides, galactoside, fructosides, etc., is preferred. In the preferred product the additional saccharide units are predominately attached to the previous saccharide unit's 2-position. Attachment through the 3-, 4-,

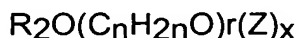
and 6- positions can also occur. Optionally and less desirably there can be a polyalkoxide chain joining the hydrophobic moiety (R) and the polysaccharide chain. The preferred alkoxide moiety is ethoxide.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 20, preferably from about 10 to about 18 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkoxide chain can contain up to about 30, preferably less than about 10, alkoxide moieties.

Suitable alkyl polysaccharides are decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-
sides, galactosides, lactosides, fructosides, fructosyls, lactosyls, glucosyls and/or galactosyls and mixtures thereof.

The alkyl monosaccharides are relatively less soluble in water than the higher alkyl polysaccharides. When used in admixture with alkyl polysaccharides, the alkyl monosaccharides are solubilized to some extent. The use of alkyl monosaccharides in admixture with alkyl polysaccharides is a preferred mode of carrying out the invention. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-
sides and tallow alkyl tetra-, penta-, and hexagluco-
sides.

The preferred alkyl polysaccharides are alkyl polyglucosides having the formula



wherein Z is derived from glucose, R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl, hydroxyalkylphenyl, and mixtures thereof in which said alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14 carbon atoms; n is 2 or 3 preferably 2, r is from 0 to 10, preferable 0; and x is from 1.5 to 8, preferably from 1.5 to 4, most preferably from 1.6 to 2.7. To prepare these compounds a long chain alcohol (R₂OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (R₁OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside.

Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (C₁₋₆) is reacted with glucose or a polyglucoside (x=2 to 4) to yield a short chain alkyl glucoside (x=1 to 4) which can in turn be reacted with a longer chain alcohol (R₂OH) to displace the short chain alcohol and obtain the desired alkyl polyglucoside. If this two step procedure is used, the short chain alkylglucoside content of the final alkyl polyglucoside material should be less than 50%, preferably less than 10%, more preferably less than about 5%, most preferably 0% of the alkyl polyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkyl polysaccharide surfactant is preferably less than about 2%, more preferably less than about 0.5% by weight of the total of the alkyl polysaccharide. For some uses it is desirable to have the alkyl monosaccharide content less than about 10%.

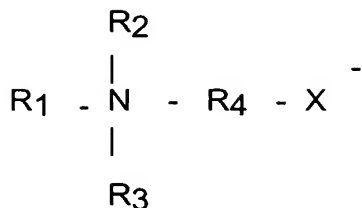
The used herein, "alkyl polysaccharide surfactant" is intended to represent both the preferred glucose and galactose derived surfactants and the less preferred alkyl polysaccharide surfactants. Throughout this specification, "alkyl polyglucoside" is used to include alkyl polyglycosides because the stereochemistry of the saccharide moiety is changed during the preparation reaction.

An especially preferred APG glycoside surfactant is APG 625 glycoside manufactured by the Henkel Corporation of Ambler, PA. APG25 is a nonionic alkyl polyglycoside characterized by the formula:

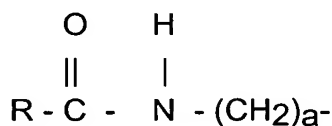


wherein n=10 (2%); n=122 (65%); n=14 (21-28%); n=16 (4-8%) and n=18 (0.5%) and x (degree of polymerization) = 1.6. APG 625 has: a pH of 6 to 10 (10% of APG 625 in distilled water); a specific gravity at 25°C of 1.1 g/ml; a density at 25°C of 9.1 lbs/gallon; a calculated HLB of 12.1 and a Brookfield viscosity at 35°C, 21 spindle, 5-10 RPM of 3,000 to 7,000 cps.

The zwitterionic surfactant optionally used in the instant composition is a water soluble betaine having the general formula



wherein X^- is selected from the group consisting of COO^- and SO_3^- and R_1 is an alkyl group having 10 to about 20 carbon atoms, preferably 12 to 16 carbon atoms, or the amido radical:

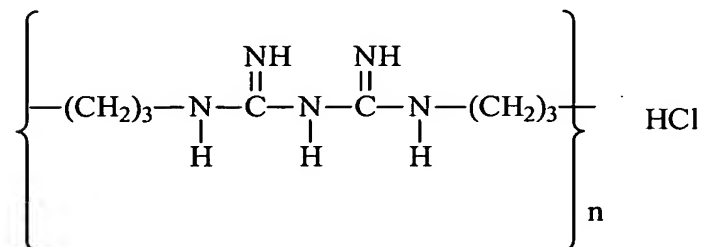


wherein R is an alkyl group having about 9 to 19 carbon atoms and a is the integer 1 to 4; R_2 and R_3 are each alkyl groups having 1 to 3 carbons and preferably 1 carbon; R_4 is an alkylene or hydroxyalkylene group having from 1 to 4 carbon atoms and,

optionally, one hydroxyl group. Typical alkyldimethyl betaines include decyl dimethyl betaine or 2-(N-decyl-N, N-dimethyl-ammonia) acetate, coco dimethyl betaine or 2-(N-coco N, N-dimethylammonia) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, lauryl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine, etc.

The amidobetaines similarly include cocoamidoethylbetaine, cocoamidopropyl betaine and the like. The amidosulfobetaines include cocoamidoethylsulfobetaine, cocoamidopropyl sulfobetaine and the like. A preferred betaine is coco (C8-C18) amidopropyl dimethyl betaine. Three preferred betaine surfactants are Empigen BS/CA from Albright and Wilson, Rewoteric AMB 13 and Goldschmidt Betaine L7.

The polyhexamethylene biguanide (PHMB) used in the instant composition has the following structure:



where the average n is comprised between 4 and 19 and more preferably is about 12. It is available under the trade name Vantocil P, Vantocil TG, Vantocil IB, Cosmocil CQ from Avecia. Another suitable commercial product is Reputex 20 wherein average n is equal to 15. However, any polymeric biguanide known may be used in this invention.

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The anionic surfactants, and polyhexamethylene biguanide hydrochloride are solubilized as a complex in the water. To the composition can also be added with water soluble hydrotropic salts which include sodium, potassium, ammonium and mono-, di- and triethanolammonium salts. While the aqueous medium is primarily water,

10 preferably the solubilizing agents are included in order to control the viscosity of the liquid composition and to control low temperature cloud clear properties. Usually, it is desirable to maintain clarity to a temperature in the range of 4°C to 20°C. Therefore, the proportion of solubilizer generally will be from 0 to 15%, preferably 0.25% to 12%, most preferably 0.5% to 8%, by weight of the detergent composition with the proportion

15 of ethanol, when present, being 5% of weight or less in order to provide a composition having a flash point above 46°C. Preferably the solubilizing ingredient will be a mixture of ethanol and either sodium xylene sulfonate or sodium cumene sulfonate or a mixture of said sulfonates or ethanol and urea. Other solubilizing agents can be ethylene glycol, propylene glycol, ethylene glycol monobutyl ether (butyl cellosolve), diethylene

20 glycol monobutyl ether (butyl carbitol), propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, triethylene glycol monobutyl ether, mono, di, tripropylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, mono, di, tripropylene glycol monomethyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene

25 glycol monopropyl ether, ethylene glycol monopentyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monopentyl ether, triethylene glycol monopropyl ether, triethylene glycol monoethyl ether, triethylene glycol monomethyl ether, triethylene glycol monopentyl ether, triethylene glycol monohexyl ether, mono, di, tripropylene

glycol monopropyl ether, mono, di, tripropylene glycol monoethyl ether, mono, di, tripropylene glycol monopentyl ether, mono, di, tripropylene glycol monohexyl ether, mono, di, tributylene glycol monomethyl ether, mono, di, tributylene glycol monohexyl ether, mono, di, tributylene glycol monopropyl ether, mono, di, tributylene glycol monoethyl ether, mono, di, tributylene glycol monopentyl ether, mono, di, tributylene glycol monobutyl ether, ethylene glycol monoacetate and dipropylene glycol propionate.

Inorganic salts such as sodium sulfate, magnesium sulfate, sodium chloride and sodium citrate can be optionally added at concentrations of 0.5 to 4.0 wt. % to control the haze of the resultant solution. Magnesium salt can be used with formulations at neutral or acidic pH since magnesium hydroxide will not precipitate at these pH levels. Various other ingredients such as urea at a concentration of 0.5 to 4.0 wt. % or urea at the same concentration of 0.5 to 4.0 wt. % can be used as solubilizing agents. Other ingredients which have been added to the compositions at concentrations of 0.01 to 4.0 wt. % are perfumes, sodium bisulfite, EDTA and HETDA. The foregoing solubilizing ingredients also facilitate the manufacture of the inventive compositions because they tend to inhibit gel formation.

The liquid compositions of the present invention have a pH of about 2 to about 9, more preferably about 5. Thus, they may comprise as an optional ingredient a source of acidity or alkalinity for the purpose of pH adjustment. Suitable sources of acidity for use herein are lactic acid, citric acid, sulfuric acid and hydrochloric acid. Suitable sources of alkalinity for use herein are the caustic alkalis such as sodium hydroxide or potassium hydroxide or also triethanolamine.

In addition to the previously mentioned essential and optional constituents of the compositions, one may also employ normal and conventional adjuvants, provided they do not adversely affect the properties of the detergent. Thus, there may be used various coloring agents and perfumes; ultraviolet light absorbers such as the Uvinuls, which are products of GAF Corporation; sequestering agents such as ethylene diamine tetraacetates; magnesium sulfate heptahydrate; pearlescing agents and opacifiers; pH modifiers, preservatives ; etc. The proportion of such adjuvant materials, in total will

normally not exceed 15% of weight of the detergent composition, and the percentages of most of such individual components will be a maximum of 5% by weight and preferably less than 2% by weight.

The instant composition liquids are readily made by simple mixing methods from readily available components which, on storage, do not adversely affect the entire composition.

The following examples illustrate liquid cleaning compositions of the described invention. The exemplified compositions are illustrative only and do not limit the scope of the invention. Unless otherwise specified, the proportions in the examples and elsewhere in the specification are by weight.

Example I

Results as shown in the following table were obtained with either paraffin sulfonate (PS), or ethoxylated alkyl ether sulfate (TEALS), or linear alkyl benzene sulfonate (LAS) in combination with PHMB at 2 different concentrations

Measure of the deposition of PHMB on ceramic tiles in presence of anionic surfactants by colorimetry - Methodology (colorimetry):

200 µl of each solution to test are deposited on 2.5x2.5cm² white ceramic tiles. After drying at room temperature, the treated tiles are rinsed with 2x10 ml deionized water.

The revelation of cationic antimicrobial agent (PHMB) is then performed with 200 µl 0.033% Indigotine (a pink anionic dye). After removing the excess of dye with 10 ml deionized water and drying of the surface, the coloration intensity is measured with a chromameter (Minolta CR200®). [L-c] is a measure of the intensity of the pink shade. The Indigotine does interact neither with the ceramic surface nor with the anionic surfactant.

Measure of the lasting antibacterial protection of the surface – Methodology:

Ceramic tiles are treated with 200 µl of the solutions to test; untreated tiles are used as reference. After overnight drying of the treatment, tiles are rinsed with 2x10 ml deionized water and let dry for 1 hour. Tiles are then inoculated in the horizontal

position for 5 hours with 200 μ l of a suspension of wild germs from hand's volunteers (mainly *Staphylococcus epidermitis*). After rinsing of the surface with 2x10 ml sterile tap water to remove the germs source, the contamination of the surface is determined by direct imprint with Tryptic Soy Agar plates (a nutritive gelified support).

- 5 Colony forming units (= cfu = microorganisms) are counted after 48 hours incubation at RT.

Results are presented in table 1 : The coloration of the tile (L-c) is the signal of the presence of the PHMB on the surface. The intensity of the coloration is related to the quantity of PHMB on the surface and to the availability of the cationic charges,
10 which is essential for the antibacterial efficiency of the active.

The presence of anionic surfactant improves the resistance to rinse of the PHMB (antibacterial agent) and ensures a better antibacterial protection of the surface.

Table 1

PHMB concentration %	Anionic surfactant concentration %	Paraffin Sulfonate		TEA ILauryl Sulfate		Linear Alkylbenzene Sulfonate	
		C.F.U./tile	L-C	C.F.U./tile	L-C	C.F.U./tile	L-C
0.09%	0	307 ±32	76	307 ±32	73	255 ±66	80
0.09%	0.01	3 ±2	61	48 ±29	60	71 ±42	65
0.09%	0.1	1 ±1	49	1 ±1	33	1 ±1	58
0.09%	0.15	57 ±15	69	7 ±2	36	no CFU	55
0.09%	0.2	175 ±17	72	77 ±12	40	not available	not available
0.09%	0.25	130 ±43	77	80 ±25	75	not available	not available
untreated surface		431 ±46	83		83	329 ±52	82
0.06%	0	492 ±86	71	452 ±94	76	329 ±63	77
0.06%	0.01	119 ±32	59	138 ±74	51	29 ±24	65
0.06%	0.1	219 ±33	73	11 ±6	17	1 ±1	58
0.06%	0.15	314 ±113	77	107 ±11	76	not available	not available
0.06%	0.2	490 ±136	80	171 ±29	80	167 ±38	70
0.06%	0.25	not available	81	not available	83	205 ±44	79
untreated surface		915 ±257	83	692 ±122	83	329 ±52	82

Example II

PHMB-anionic surfactant in a spray cleaner composition

Test methodology is described under example I “Measure of the lasting antibacterial protection of the surface”

Cleaning composition:		
	Paraffin sulfonate	0.1%
	Neodol 91-8	1.25%
10	Neodol 91-2.5	0.25%
	Cocoamidopropyl betaine	0.45%
	PnB	0.85%
	DPGME	2%
	Ethanol	1%
15	Fragrance	0.45%
	pH 5.5 with citric acid	

Results

	Test Products	CFU*/tile average on 3 replicates
20	Cleaning composition	305±17
	Cleaning composition + PHMB 0.06%	34±29

* CFU = colony forming unit